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Mixed Ligand Chelates of Cu(II), Zn(II), Ni(II) & Co(II) with Nitrilotriacetic Acid as the Primary Ligand & 3,5-Dinitro- & 3,5-Dibromo-salicylic Acids as Secondary Ligands

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Binary and ternary complexes of the type M-L and M-NTA-L [M = Cu(II), Zn(II), Ni(II) or Co(II); NTA = nitrilotriacetic acid; and L = 3,5-dinitrosalicylic acid (DNSA) or 3,5-dibromosalicyclic acid (DBSA)] have been examined *p*H-metrically at 25° and μ = 0·1*M* ($NaClO_4$) in 50% (v/v) aq. ethanol. The logarithms of the values of formation constant for M-DNSA (corresponding to the first step) and M-NTA-DNSA systems [M = Cu(II), Zn(II), Ni(II) and Co(II)] are 7·63, 4·47, 5·01, 4·57; and 4·28, 3·15, 3·87, 3·11 respectively, while for M-DBSA and M-NTA-DBSA systems [M = Cu(II) and Zn(II)] these values are 8·90, 7·46; and 6·04, 5·09 respectively. The second step formation constants of the binary complexes could be evaluated only in the case of Cu(II) complexes of DNSA and DBSA and the values are 5·03 and 6·80 respectively.

BINARY complexes of 3,5-dinitrosalicylic acid (DNSA)[1-4] and 3,5-dibromosalicylic acid (DBSA)[2] have been studied with a number of metal ions in aqueous medium, but mixed ligand complexes with these ligands have not been investigated. We report here the results of our studies on mixed ligand complexes of Cu(II), Zn(II), Ni(II) and Co(II) with nitrilotriacetic acid (NTA) as the primary and DNSA and DBSA as secondary ligands in 50% (*v/v*) aq. ethanol employing *p*H-metric titration technique[5,6]. Under identical conditions the binary metal complexes of DNSA and DBSA have also been investigated.

Materials and Methods

All the reagents were of analytical grade.

Solutions of Cu(II), Zn(II), Ni(II) and Co(II) perchlorates were prepared and standardized according to known methods[7]. Suitable aliquots of these solutions were separately diluted and perchloric acid added if necessary to obtain 0·01*M* metal perchlorate in 0·02*M* perchloric acid.

Standard solutions of 0·098*M* NaOH, 0·02*M* $HClO_4$ and 1·0*M* $NaClO_4$ were prepared as usual.

Stock solutions of 0·005*M* of the ligands NTA (in water), DNSA (in ethanol) and DBSA (in ethanol) were prepared by direct weighing.

Procedure — *p*H-measurements were performed at 25° using Leeds & Northrup *p*H-meter with glass-calomel electrodes. The medium was 50% (*v/v*) aq. ethanol and ionic strength 0·1*M* ($NaClO_4$).

For the study of binary M-L systems, three mixtures[8] (total volume 50·0 ml) (*A*) acid, (*B*) ligand, and (*C*) chelate were prepared. The metal ion solutions contained a known amount of free acid to prevent hydrolysis. In mixtures *A*, *B* and *C* the total quantity of free acid was kept the same. The concentrations were: $N°=0·098M$; $E°=0·002M$, $TC^{\circ}_{L}=0·001M$; and $TC^{\circ}_{M}=0·0002M$ (symbols have their usual meanings[5]). Mixtures *A*, *B* and *C* were individually titrated against standard alkali and the plots of *p*H versus volume of alkali gave the titration curves.

For the study of the ternary M-NTA-L systems, the mixtures prepared (total volume 50·0 ml) were: (*D*) acid+NTA; (*E*) mixture *D*+metal solution; (*F*) acid+DNSA (or DBSA) and (*G*) mixture *E* + DNSA (or DBSA). In titrations of mixtures *E* and *G*, no perchloric acid was added as the metal solution already contained the required amount of acid. In mixture *F* an extra amount of perchloric acid, equivalent to the acidity of NTA taken in mixture *E*, was added to compensate for the three protons liberated as a result of complexation of NTA with metal ions. The concentrations were: $TC^{\circ}_{L}=0·001M$, $TC_{NTA°}=TC_{M.NTA°}=TC_{M°}=0·001M$, where $TC_{NTA°}$ and $TC_{M.NTA°}$ are total initial concentrations of NTA and M.NTA complex respectively. Other symbols have their usual meanings. $N°$ and $E°$ in titration mixtures were the same as in binary systems and an allowance for extra acid taken in mixture *F* was made in calculations. These mixtures were separately titrated against NaOH and titration curves *D*, *E*, *F* and *G* for the systems were obtained. Fig. 1 shows the curves for Cu(II)-NTA-DNSA system.

Calculations

M-L systems — The titration curves were used to evaluate $\bar{n}_A$ (average number of protons associated with the ligand DNSA or DBSA); $\bar{n}$ (average number of ligand DNSA or DBSA molecules attached per metal ion); and *p*L (free ligand exponent). From these data, the proton-ligand and metal ligand stability constants were obtained (Table 1).

The absence of polynuclear species, etc. was confirmed by repeating the experiments using several concentrations of the reactants, where the results obtained were identical. Precipitation occurred

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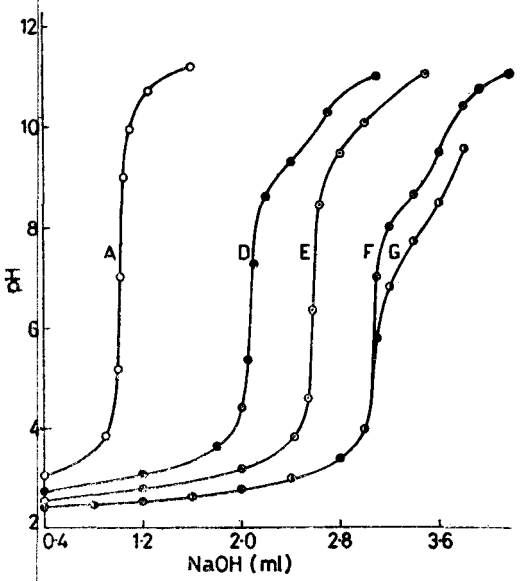

Fig. 1 — Titration curves for Cu(II)-NTA-DNSA systems [Acid (A); NTA (D); Cu(II)-NTA (E); DNSA (F) and Cu(II)-NTA-DNSA (G)]

even before the stage of 1:1 or 1:2 [only in the case of Cu(II)] complexation was complete, and no studies beyond this stage were possible. Hence, the hydroxo species likely to be formed after this stage could not be considered.

M-NTA-L systems — From curves *A*, *D* and *E* (Fig. 1) it is noted that complete formation of $(M.NTA)^-$ specie takes place at a pH$\approx$4, which remains stable at higher pH values. Curve *G* shows a displacement with respect to curve *F* along the volume axis at a pH above the complete formation of $(M.NTA)^-$ specie. It may thus be assumed that it is only (M.NTA)-species which is involved in the process of complexation with the secondary ligand DNSA or DBSA. As such, the horizontal distances between curves *F* and *G* were measured and used for the calculation of $\bar{n}_{mix}$ (average number of secondary ligand molecules attached per $(M.NTA)^-$ ion using Eq. (1).

$$\bar{n}_{mix} = \frac{(v_G - v_F)\ (N^\circ + E^\circ)}{(V^\circ + v')\ \bar{n}_{A^\circ}.\ TC_{M.NTA^\circ}} \qquad \ldots(1)$$

Table 1 — Stability Constants of Binary (M-L) and Ternary (M-NTA-L) Chelates in 50% (v/v) Aq. Ethanol at 25° and $\mu = 0{\cdot}1M$

Cation	log K_1	log K_2	log $K^{M.NTA}_{M.NTA.L}$
	Secondary ligand: DNSA		
H^+	8·47	—	—
Cu(II)	7·63	5·03	4·28
Zn(II)	4·47	—	3·15
Ni(II)	5·01	—	3·87
Co(II)	4·57	—	3·11
	Secondary ligand: DBSA		
H^+	11·80	2·76	—
Cu(II)	8·90	6·81	6·04
Zn(II)	7·46	—	5·09

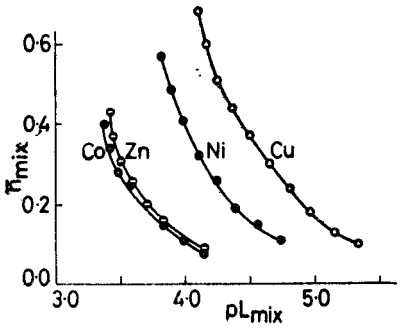

Fig. 2 — Formation curves for M-NTA-DNSA systems

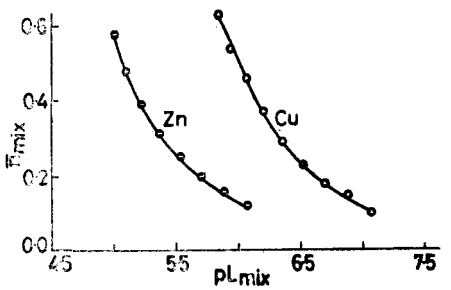

Fig. 3 — Formation curves for M-NTA-DBSA systems

where v_G and v_F are the volumes of alkali consumed to reach the same pH value in the curves *G* and *F* of the mixed ligand system and $TC_{M.NTA^\circ}$ = total initial concentration of $(M.NTA)^-$ complex which is equivalent to the initial metal ion concentration taken in mixture *E*. All other symbols have their usual meanings[5]. Values of n_A at different pH values were available from the data of binary complexing system. From the values obtained for $\bar{n}_{mix}$ free ligand exponent pL$_{mix}$ was calculated using the Eq. (2).

$$p\mathrm{L}_{mix} = \log_{10}\left[\frac{\sum_{n=0}^{j}\beta_n^H\left(\frac{1}{\text{antilog }\bar{B}}\right)^n}{TC_{L^\circ} - \bar{n}_{mix}.TC_{M.NTA^\circ}}.\frac{V^\circ + v_G}{V^\circ}\right] \qquad \ldots(2)$$

The parameters $\bar{n}_{mix}$ and pL$_{mix}$ were treated similarly as in binary systems whereby formation curves were obtained (Figs. 2 and 3). The values of formation constants for various systems are recorded in Table 1.

Results and Discussion

Binary Systems

Proton-ligand systems — The formation curves for the ligands DNSA or DBSA exhibit a wave like shape, suggesting that the dissociation of proton from the phenolic and carboxylic groups occurs in two distinct steps. Protonation constants (log K_2) corresponding to carboxylic group of DNSA could not be determined as it gets completely dissociated under experimental conditions, whereas the data corresponding to the protonation for the phenolic group (log K_1) could be calculated reliably. Values of both the protonation constants in the case of DBSA could be determined.

Usually presence of electron withdrawing nitro group in phenols or benzoic acids increases their acidity. On the other hand, bromo group not only exerts an electron withdrawing inductive effect but also an electron donating mesomeric effect, when located at *ortho* or *para* positions to phenolic OH or carboxylic COOH group. Further, the inductive effect is more pronounced with nitro group than with the bromo group[9]. The influence of the location of nitro group in DNSA and bromo group in DBSA thus results in the protonation constants of DNSA being lower than those of DBSA (Table 1).

Metal-ligand systems — Amongst various binary systems studied (Table 1) it was noted that only Cu(II) formed both 1:1 and 1:2 complexes in two distinct steps, both with DNSA and DBSA, while Zn(II) formed only 1:1 complex. Ni(II) and Co(II) formed 1:1 complexes with only DNSA. 1:2 complex in such systems could not be examined due to precipitation accompanied by opacity, turbidity, etc. In Ni(II)-DBSA and Co(II)-DBSA systems the formation of the complexes seemed to be doubtful as the $\bar{n}$ values were too low to provide any reliable value of the stability constants and so these systems were not worked out further.

The order of stabilities (Table 1) in all the binary systems studied follow the expected order:

$$Co(II) < Ni(II) < Cu(II) > Zn(II)$$

Ternary Systems

Table 1 indicates that the value of log $K^{M.NTA}_{M.NTA.L}$ ($K^{M.NTA}_{M.NTA.}$ = stoichiometric mixed ligand formation constant in M-NTA-L systems) is less than log K_1 and is even less than log K_2 (K_1 and K_2 are the first and second step formation constants of the binary metal complexes of the secondary ligands). This behaviour can be explained on the basis of coulombic interaction between various ligand anion species present. In the mixed ligand complex formation there is a repulsion between two negative charges from the secondary ligand anion and three negative charges from the NTA anion. The repulsion would obviously be more than the repulsion encountered by two negative charges each from the two secondary ligand anions in the formation of ML_2 species, ultimately resulting in log K_2 > log $K^{M.NTA}_{M.NTAL}$. No such interaction is possible in the formation of ML species. Log K_1 > log K_2 is well established, which then justifies the final order:

$$\log K_1 > \log K_2 > \log K^{M.NTA}_{M.NTAL}$$

The observations of Bhattacharya *et al.*[10,11] in several other ternary systems involving NTA as a primary ligand are in agreement with our findings.

In all the ternary systems studied, the order of stability of mixed ligand complexes with respect to the metal ions was found to be Co(II) < Ni(II) < Cu(II) > Zn(II), which is same as in the corresponding binary (M-L) systems.

Acknowledgement

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